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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Hydrogen soil deposition at an urban site in Finland" *by* M. Lallo et al.

M. Lallo et al.

marko.lallo@fmi.fi

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Author Comments #2 Anonymous Referee #2 Received and published: 3 September 2009

*Lallo et al. calculated H2 soil deposition velocities for the region of Helsinki, Finland with three different methods. They derived deposition velocities directly from chamber measurements, by applying the 222Rn tracer method and with a two-dimensional model. All three methods are described and results are compared with each other also with respect to soil temperature, air temperature, and soil moisture content. Though there have been a few recent studies with a similar scope, this paper is of interest as the soil deposition is the largest sink process for molecular hydrogen and due to the variety of soil types, climates the global and seasonal picture still not completely understood. The paper is scientifically sound and within the scope of ACP. After some

minor corrections, I recommend this paper for publication in ACP.

Some specific comments:

*P14874 L 5: . . . estimate the vd [space character] in . . .

Correction: Radon tracer method was used to estimate the vd in nighttime when photochemical reactions . . .

*P14874 L 6: . . .concentrated in the shallow boundary layer . . .

Correction: . . .were minimal and radon gas was concentrated in the shallow boundary layer due to exhalation from soil.

*P14874 L 11-12: maybe better ? ". . . (2D model). . ."

Answer: I have consistently used the word 'two-dimensional' throughout the manuscript.

*P 14874 L 13: . . . revealed a relation between the one week

Correction: Both models and chamber measurements revealed a relation between the one week cumulative rain sum and deposition velocity.

*P14874 L 15: maybe better? When precipitation events occurred a few days before chamber measurements, lower vd values were observed.

Correction: When precipitation events occurred a few days before the chamber measurements, lower vd values were observed.

*Introduction: Please add some information concerning H2, seasonality (latitudinal differences!), budget, sources and sinks. Just to point out the importance of the soil sink especially for the northern hemisphere! Furthermore, maybe you could give some more background information on recent findings about the H2 deposition velocities (dependence on temperature, snow cover, soil parameters, for example you already mentioned Schmitt et al., Lallo 2008), just like you did for the radon exhalation (see

P14875, L 22 ff).

Answer: Following sentences will be added to manuscript:

Ehhalt and Rohrer (2009) reported based on the findings of Price et al. (2007) and Novelli (1999). The hydrogen mixing ratio is asymmetrically distributed between the hemispheres. In Northern Hemisphere (NH) it reaches 490 ppb at 80°N. In Southern Hemisphere (SH) mixing ratio reaches 535 ppb at 88°S. Barnes et al. (2003) observed a seasonal cycle for mixing ratio of atmospheric hydrogen in Harvard forest with the maximum in winter-spring months (February to June) and short minimum in September-October. Simmonds et al. (2000) observed a similar seasonal cycle with the highest mixing ratio during the spring months of March to May and the lowest values in September to November. Rhee et al. (2006) estimated the total budget for NH, where total hydrogen sources were 69 Tg(H2) a-1 and 62 Tg(H2) a-1 of the total sources were consumed by soils. For SH total hydrogen sources was estimated to be 38 Tg(H2) a-1 and 26 Tg(H2) a-1 being consumed by the soils. Globally atmospheric sink and source budget vary between 136 and 155 Tg(H2) a-1 (Hauglustaine and Ehhalt 2002, Novelli, 1999). Soil moisture is coupled with the soil temperature. High H2 deposition velocities are usually associated with low soil moisture (Schmitt, 2009), when soil temperature is high. A thick snow layer hinders the gas permeation into soil surface lowering the H2 deposition velocity values (Lallo et al. 2008).

*P14875 L 22: . . . which depends mainly . . .soil porosity. High soil moisture . . .. (Levin et al.). The latitudinal distribution. . .

Correction: The results are dependent on radon exhalation rate, which depends mainly on grain size distribution and soil porosity. High soil moisture/water content is also known to hinder the radon exhalation (Levin et al., 2002). The latitudinal distribution of 222Rn flux is examined by Conen and Robertson (2002).

*P 14876 L 5 ff: maybe better: The closest roads with a high traffic volume, Hämeentie (44700 cars per day) and Mäkelänkatu (45000 cars per day), were in a minimum

distance of 350 m and 700 m, respectively.

Correction: The closest roads with a high traffic volume Hämeentie (44700 cars per day) and Mäkelänkatu (45 000 cars per day) were in a minimum distance of 350 m and 700 m, respectively.

*L 9: ". . .the soil texture of the measurement site : : : provided by the Geological Survey. . ."

Correction: The soil texture of the measurement site including surface vegetation is fine sandy till (sandy loam) according to maps provided by the Geological Survey of Finland, (a geological map available at: http://geomaps2.gtk.fi/geo/, 2009).

*L 12 ff: "The detailed. . .determined in laboratory studies (Soil. . .) to be . . ."

Correction: The detailed soil type was determined in laboratory studies (Soil Analysis Service in Mikkeli, Finland) to be gravely sandy loam (fractionated soil type) in the first 7 cm.

*Concerning your measurement technique with the syringes: How do you account for the "missing air mass" in the closed chamber? Does it not generate negative pressure when you draw the air sample from the chamber?

Answer: The chamber headspace volume is very large (over 100 L) compared to syringe volume (20 mL). Approximately, 0.4 L(syringe flushing and 5 samples) were sucked during one measurement cycle. Small negative pressure difference is unavoidable, but it effects could be minimized using large chamber volume and short closing time as described by (Davidson et al. 2002).

*P 14877 L 14: ". . .with a residence time of ca. 1 s."

Correction: Sample air was first transferred through plastic tubing at flow speed 10 m s-1, with a residence time ca. 1 s.

*L 15 ff: "A side flow. . .. . .filtered with a 1.0. . ..and flushed through a stainless. . .to a

flow restrictor. . ....200 cm3 min-1 to the analyzer."

Correction: A side flow to hydrogen analyzer was filtered with a 1.0 um Gelman filter and flushed through a stainless steel tubing to a flow restrictor and pressure relief valve , which was adjusted to pass about 200 cm3 min-1 to the analyzer.

*L 19: ". . .molecular hydrogen passes through the mercury. . .(HgO)"

Correction: After chromatographic separation of sample air, molecular hydrogen passes through the mercury oxide (HgO) bed.

*L 20: H2 reduces HgO to gaseous Hg which is then detected by UV absorption.

Correction: H2 reduces HgO to gaseous Hg, which is then detected by UV absorption.

*L 24 – 28: check the time, you switch between present tense and past tense.

Correction: Four ambient air samples were measured during one measurement cycle, after which a working standard was included in the cycle. Each analysis took 5 min The system was calibrated according to four standards (scale 400–700 ppb) acquired from Max-Planck Institute in Jena. The reproducibility of RGA5 instrument was estimated by taking into account ten consecutive working standard samples, and it was found to be 1.1% (range 915–950 ppb). More details are included in a companion article (Aalto et al. 2009).

*L 28: What is the precision of the instrument at ambient levels of H2 ? Answer: The reproducibility at ambient levels was obtained using the calibration samples (400-700 ppb). Maximum standard deviation during the calibration was 1.5%.

*P 14878 L 1: Is it really linear ? In my experience the RGD often exhibits a non-linear behaviour. What did you correlate here ? height / area versus mixing ratio ?

Answer: The linearity was checked within the broad range (200 - 2000 ppb).In this range the squared correlation (R2) for linear fit was . 0.995 and for the second order fit 0.997. Within the atmospheric range (400-700 ppb) the squared correlation for linear

fit was 0.973 and for the second order 0.974. We correlate a peak area against mixing ratio.

*L 7: ". . .radioactive equilibrium. . ."

Correction: The determination of radon is based on the short-lived 222Rn progeny assumed to be in radioactive equilibrium.

*L 8: "... is similar as described. . ." Correction: The analysis method is similar as described in Paatero et al. (1998)

*L 16: ". . .follows an exponentially. . ." In the following lines some more articles, indefinite and definite, are missing – please check the paper!

Correction: The hydrogen concentration decrease inside a closed-chamber follows an exponentially decreasing function. Missing articles are also checked

*L 24: Would it not be 0 ppb H2 in the chamber without a H2 source ? Answer: A three hour measurement period was not long enough to achieve 0 ppb, but it showed a decreasing trend towards 0 ppb. There was not e.g.clover vegetation in the field site, which could produce hydrogen.

*P 14879 L 6: ". . .originates. . ."

Correction: This indicates that the changes in trace gas mixing ratios originates from the variability of diurnal atmospheric conditions rather than short term changes of trace gas emissions (Levin et al., 1999).

*L 9: ". . .the nocturnal boundary layer"

Correction: The height of the nocturnal boundary layer is usually a few hundreds of meters, in which radon is accumulating.

*L 13: Switch position of sentences.1.) "The photochemical reaction. . .during nighttime." 2) "Thus, the major sink is ...., while the only source process for 222Rn is the

exhalation from the soil. The H2 flux can be calculated. . ."

Correction: The photochemical reactions, e.g. due to hydroxyl radical formation from ozone, are not significant in low irradiance conditions during nighttime, thus the major sink of hydrogen is soil and hydrogen is consumed in the first few centimeters of the soil (Schmitt et al., 2008), while the only source process for 222Rn is the exhalation from the soil

*P 14880 L 5: "the model is based on a three-dimensional atmospheric model described in Aalto et al. (2006)."

Correction: The model is based on a three-dimensional atmospheric model described in Aalto et al. (2006)

*L 7: What does it mean that you describe the topography by "one specific type" ?

Answer: The vegetation model was simplified to one type, which have equal features with relation to H2. A simplified model was done to reduce time consuming complex calculations.

*L 13-15: What is the model resolution? Answer: The model resolution is 1 km (ten grid boxes in ten kilometer range).

*L 25: ". . .radon tracer model. . ." Do you mean method ? ff: maybe re-formulate the description on how you calculate the deposition velocities ? To my understanding: You solve the equations for H2 vd and the Rn exhalation rate (in the model) in order to minimize the differences between the observed H2 / Rn profiles and the model out put – is that correct ?

Correction: 'As in the case of radon tracer method, the nighttime simulations were made to avoid indirect photochemical degradation of hydrogen.'

Yes, We solve the equations for H2 vd and radon, then we minimize the differences between modeled and observed values. Following sentence is also added to manuscript:

'The model minimizes the difference between the modeled and observed values.'

You use BL as an abbreviation for boundary layer, that is ok, however, you should introduce the first time you mention it.

Correction: On contrasting winter night conditions (-15 °C) in 10 February 2007, the model simulated the first inversion at 75 m model level, and second at 198m level, while ceilometer results indicated 70-200 m for a boundary layer (BL) height.

*P14882 ff: How did you determine your error bars? I am missing sensitivity study for all methods.

Answer: All error bars were calculated as standard error of the mean, except mentioned otherwise. Chamber error bars were calculated by averaging all three or four repetitions. Sensitivity studies related to syringe sampling from the chamber have been made in a three-hour field test. Three consecutive samples were taken to represent one sampling moment. According to this test all points were well distributed along an exponentially decreasing curve. Soil temperature is a slowly changing feature and it takes usually several days to see the changing trend. This is also the case with soil moisture. Radon tracer method is sensitive to changes in radon emissions and its applicability is regional. Radon gas is accumulating in to a nighttime boundary layer. For this reason a stable nocturnal layer and low wind conditions are needed. Typical range is about tens of kilometers to over one hundred. The hydrogen flux calculation in the two-dimensional model is dependent on boundary layer height estimation. This could produce error of 10% to a few tens. A minor source of error is the vegetation layer, which is modeled as a single uniform layer.

*When you refer to your Figures please add some information on which data you are referring to (describe the symbols, colours etc.) in the text and in the caption of the respective Figures (1-6). Furthermore, when you refer to single dates, could you maybe mention or highlight the respective points in the Figures (if it is possible) ?

Correction: A more detailed text and symbol reference is added to figures, if needed. Single dates (e.g. 24 Aug 2007 and 30 10 2007, 2 February 2007) are marked to figures when text reference. Figure 3 is revised and divided to three separate pictures (abc) Figure 3ab is added to author comments (see below).

*P14885 L 14 ff: What does this imply for the comparability of your data ?

Answer: The uncertainty range of radon tracer and two-dimensional results in hydrogen vd values are larger than chamber vd values. The results of simulation methods are between the range 0.00 mm s-1 to 0.90, which follows also the results of chamber based vd values. Only two highest radon tracer points (0.90 mm s-1) are higher than chamber results. Although error bars are larger in both models, model points are comparable with the chamber results.

*P14886 L 20: "However, it is not probable. . ." Maybe you could illustrate this more in a kind of sensitivity study (see comment above).

Answer: When nocturnal nighttime layer is formed, radon accumulates evenly in the layer. This shallow inversion layer is formed usually in low wind situations. In daytime, boundary layer height increases and radon is mixed in to larger volume and it is more unevenly distributed.

*P14887 L 21: ". . .dependency above zero. . ."

Correction: Among both models, results did not show clear temperature dependency above zero temperatures.

*L 26: ". . .is capable of drying the top soil. . ."

Correction: A strong solar irradiation during summer (May to July) above 600 W m-2 is capable of drying the top soil layer allowing higher soil uptake.

*P14888: Can instrumental problems be ruled out for the different H2 vd values on August 24, 2007 and October 30, 2007 ?

Answer:

The hydrogen instrument was working properly on 24 August and 30 October 2007 The concentration record on 24 August 2007 was good. Also on 30 October the record was good

References: Davidson, E.A., Savage, K., Verchot, L.V., Navarro, R. (2002), Minimizing artifacts and biases in chamber-based measurements of soil respiration, Agric. For. Meteorol.,113, 21-37.

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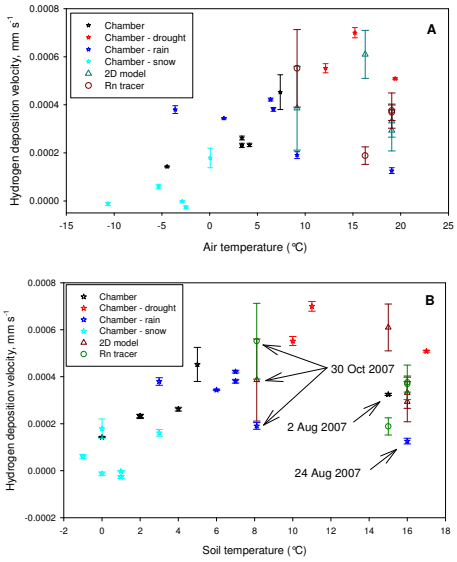

Fig. 1. 'Fig.3 (a) The dependency of measured and four modeled hydrogen deposition velocity values (a) to air and (b) to soil temperature of chamber measurements and...'